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Role of methyl group number on SOA formation from monocyclic aromatic hydrocarbons photooxidation under low-NO_X conditions

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Table S1 Aromatic hydrocarbon physical properties and rate constant

Compound	Vapor Pressure[a]	Boiling Point[b]	k_{OH}[c]	SAPRC-k_{OH}[d]
Benzene	75	80	0.139	0.122
Toluene	21	111	0.563	0.558
m-Xylene	9	139	2.31	2.31
1,2,4-trimethylbenzene	2.1	170	3.25	3.25
1,2,4,5-tetramethylbenzene	5.28E-1	193	5.55	4.10
Pentamethylbenzene	3.48E-02*	232	10.3	7.63
Hexamethylbenzene	8.60E-04	265	11.3	11.3

Note: a) vapor pressures are referred to Chemispider in unit mmHg at 25 °C; b) boiling points are referred to Chemispider in unit °C; c) OH reaction rate constants are refer to Calvert, et al, 2002; Atkinson and Arey, 2003; Aschmann, et al, 2013 in unit 10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 25 °C. d) OH reaction rate constants used in SAPRC-11 model in unit 10^{-11} cm^3 $molecule^{-1}$ s^{-1} at 25 °C ; * Experimental vapor pressure measured at 20°C, An estimated vapor pressure at 25°C is 3.56e-2 according to Chemispider. .

Table S2 Experimental conditions for additional *m*-xylene experiments from Song, et al. (2005)

ID	HC/NO[a]	NO[b]	HC[b]	ΔHC[c]	M_0[c]	Yield
104A	10.1	64.4	81.3	328	21.7	0.07
104B	29.3	21.4	78.4	281	20.4	0.07
107A	26.0	89.6	291	1029	146	0.14
129A	15.1	45.5	86	336	21.9	0.07
149A	13.3	50.2	83.6	342	52.8	0.15
164A	12.4	44.0	68.0	271	16.8	0.06
164B	12.2	44.1	67.5	270	14.6	0.05
217A	36.8	8.90	40.9	155	9.80	0.06
217B	35.9	8.70	39	153	7.90	0.05
219A	63.7	7.00	55.7	165	9.20	0.06
219B	67.5	6.60	55.7	166	9.30	0.06
288A	63.1	7.00	55.2	183	9.00	0.05
290A	31.1	15.3	59.5	229	9.00	0.04
293A	29.9	13.7	51.2	189	9.20	0.05
368A	17.9	21.0	47.0	149	6.90	0.05
485A	17.5	43.3	94.7	353	37.2	0.11
485B	16.7	45.0	93.7	349	40.4	0.12
488A	15.5	46.2	89.6	341	29.5	0.09
492A	13.6	44.3	75.2	296	29.1	0.10
492B	13.5	44.8	75.5	298	29.7	0.10
566A	14.0	48.3	84.5	337	48.2	0.14
566B	13.3	48.0	79.8	318	48.4	0.15
758A	47.5	11.4	67.7	158	13.5	0.09
820A	30.2	20.7	78.1	260	17.0	0.07

Note: a) Unit of HC/NO are ppbC:ppb; b) Unit of NO and HC are ppb; c) Unit of ΔHC and M_0 are $\mu g \cdot m^{-3}$

Table S3 Average radical concentrations throughout photooxidation

Run ID	RO_2[a]	HO_2[a]	OH[b]	HO_2*RO_2[c]	HO_2/RO_2	NO/HO_2	OH/HO_2[d]	NO_3[a]
1236A	12.9	23.5	4.9	530	2.7	4.9E+03	3.3E-02	1.8
1236B	1.30	4.4	4.7	30.4	3.9	5.9E+05	3.6E-01	8.3
1237A	15.2	20.8	7.6	488	2.3	3.1E+04	1.4E-01	1.9
1237B	13.7	20.7	5.6	416	2.3	2.3E+02	1.2E-02	0.9
1223A	10.5	24.0	4.7	376	2.7	1.5E+04	6.2E-02	1.7
1618A	9.50	107.2	5.5	1194	13.5	3.1E+01	1.1E-03	6.2
1223B	10.0	16.4	7.0	508	3.2	1.7E+08	4.3E+01	5.6
1101A	15.7	19.3	6.8	335	1.4	5.8E+01	7.8E-03	4.0
1101B	16.3	18.5	5.0	320	1.2	8.9E+00	3.8E-03	1.4
1102A	12.9	17.3	10	313	1.7	1.6E+04	1.2E-01	16.2
1102B	13.8	17.5	8.7	328	1.6	1.0E+03	2.8E-02	10.5
1106A	7.30	12.3	10	118	1.9	8.1E+02	3.9E-02	16.3
1106B	9.30	14.5	7.9	144	1.6	1.5E+01	8.2E-03	6.0
1468A	23.8	24.5	3.9	716	1.3	6.3E+01	3.2E-03	11.8
1468B	26.4	26.3	4.1	740	1.0	4.6E+01	3.1E-03	4.8
1193A	11.0	12.3	3.1	185	1.3	1.5E+06	1.8E+00	14.0
1193B	9.00	11.6	2.8	141	1.4	3.2E+05	4.2E-01	18.7
1191A	19.1	15.8	5.8	449	1.2	4.5E+05	3.4E-01	32.0
1191B	10.8	12.4	2.4	190	1.5	3.8E+04	5.1E-02	18.5
1516A	18.6	23.1	3.1	465	1.3	1.5E+01	2.0E-03	2.4
1950A	11.7	20.6	4.5	267	1.8	7.2E+01	4.3E-03	38.4
1950B	13.3	22.0	4.6	326	1.7	4.6E+01	3.7E-03	37.1
1117A	13.1	15.8	1.7	220	1.3	1.2E+01	1.5E-03	7.3
1117B	9.80	14.6	2.5	172	1.6	1.9E+02	4.7E-03	34.9
1119A	12.5	18.8	5.3	300	1.7	2.7E+03	1.7E-02	89.0
1119B	12.2	17.3	4.0	296	1.9	2.9E+03	1.7E-02	68.6
1123A	15.9	15.1	1.7	274	1.1	6.8E+01	2.2E-03	2.9
1123B	15.8	18.6	2.5	321	1.2	7.7E+01	3.0E-03	23.2
1126A	17.3	17.6	1.7	324	1.1	1.7E+01	1.5E-03	4.3
1126B	30.0	24.8	7.5	841	1.0	3.2E+01	3.8E-03	33.7
1129B	11.2	15.4	4.3	199	1.6	5.6E+01	4.9E-03	24.0
1531A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
1603A	40.9	21.8	1.6	971	0.7	2.3E+01	9.5E-04	0.6
1603B	38.9	20.4	1.6	925	0.8	7.7E+01	1.3E-03	0.6

2085A	31.5	28.3	1.2	971.5	1.1	3.2E+01	6.7E-04	2.2
2085B	27.4	22.7	0.6	642.2	1.0	3.7E+00	3.2E-04	0.5
1488A	N/A	N/A	N/A	N/A	N/A	N/A	N/A	N/A
1521A	24.7	23.5	0.8	621	1.0	4.7E+01	5.4E-04	1.2
1627A	27.8	23.0	1.0	702	1.0	5.7E+01	6.9E-04	1.0
1627B	15.5	22.2	2.1	439	1.6	4.0E+03	4.9E-03	47.5
1557A	10.1	16.7	0.2	171	1.7	1.6E+00	9.3E-05	0.5
2083A	13.5	15.6	0.9	280	1.3	1.6E+06	6.0E-01	1.1
2083B	10.0	17.0	1.2	213	1.8	4.0E+02	2.0E-03	13.8

Note: average radical concentrations are calculated by dividing time integrated radical parameters with photooxidation time; average radical concentration throughout photooxidation a) in 10^6 molecules·cm^{-3}; b) in 10^8 molecules·cm^{-3}; c) in 10^{16} molecules·cm^{-3}; d) average radical ratio throughout photooxidation in 10^3

Table S4 Correlation between SOA yields and average radical concentrations

	RO_2	HO_2	OH	HO_2*RO_2	HO_2/ RO_2	NO/HO_2	OH/HO_2	NO_3
Yield	-0.243	0.169	0.459	0.067	0.261	0.294	0.292	-0.237
p-value[a]	0.125	0.292	0.003	0.678	0.099	0.062	0.064	0.136

Note: a) P-values range from 0 to 1, 0-reject null hypothesis and 1 accept null hypothesis. Alpha (α) level used is 0.05. If the p-value of a test statistic is less than alpha, the null hypothesis is rejected

Table S5 Correlation among SOA density, volatility (VFR), SOA chemical composition and methyl group number

	Density	VFR_{end}[a]	f_{44}	f_{43}	H/C	O/C	OS_c	Methyl[c]
Density	-	0.715	0.790	-0.839	-0.756	**0.873**	0.834	-0.943
p-value[b]	-	0.071	0.034	0.018	0.049	0.01	0.02	0.001
VFR_{end}[a]	0.715	-	0.768	-0.896	-0.905	**0.937**	0.932	-0.838
p-value[b]	0.071	-	0.044	0.006	0.005	0.002	0.002	0.0019

Note: a) VFR_{end} volume remaining fraction at the end of photooxidation; b) P-values range from 0 to 1, 0-reject null hypothesis and 1 accept null hypothesis. Alpha (α) level used is 0.05. If the p-value of a test statistic is less than alpha, the null hypothesis is rejected; c) Methyl group number is used for statistical analysis

Table S6 Vapor pressure predication of selected benzene photooxidation products

Formula	Reaction pathway	Predicted $logP_{vap}$[a]
$C_6H_6O_5$	S_1, Bicyclic peroxide	-3.83E+00

$C_6H_6O_8$	S_1,Bicyclic peroxide	-6.39E+00
$C_8H_{10}O_{10}$	S_3, Oligomerization, c-2-1	-1.13E+01
$C_8H_{10}O_9$	S_3, Oligomerization, c-1-1	-7.47E+00
$C_6H_8O_6$	S_3, Oligomerization, c-2-1, with glyoxal	-6.92E+00

Note : a) Prediction is based on Pankow and Asher 2008, $\log P_{vap}$ is in the unit of log(atm)

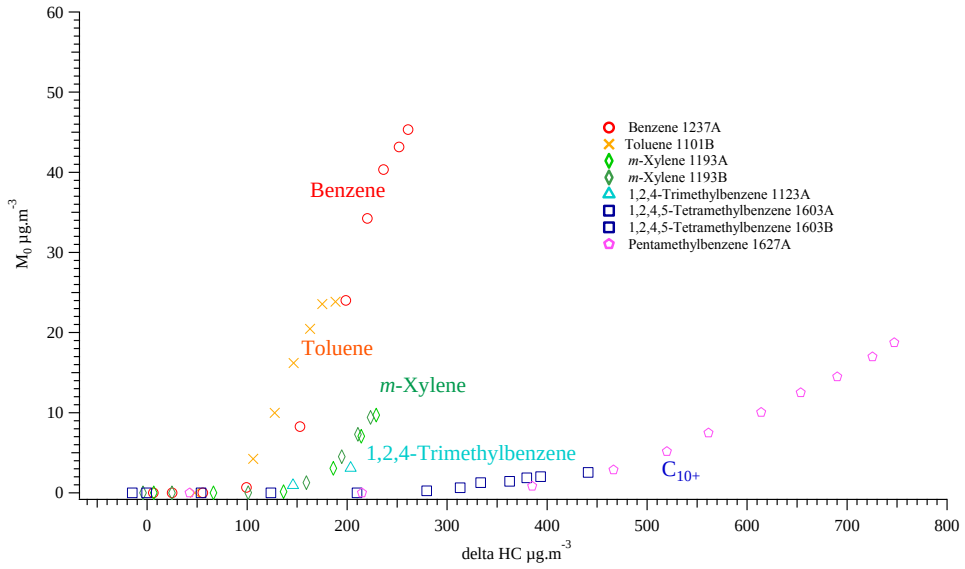


Fig. S1. Aromatic SOA growth curve (particle concentration M_0 vs. hydrocarbon consumption ΔHC)

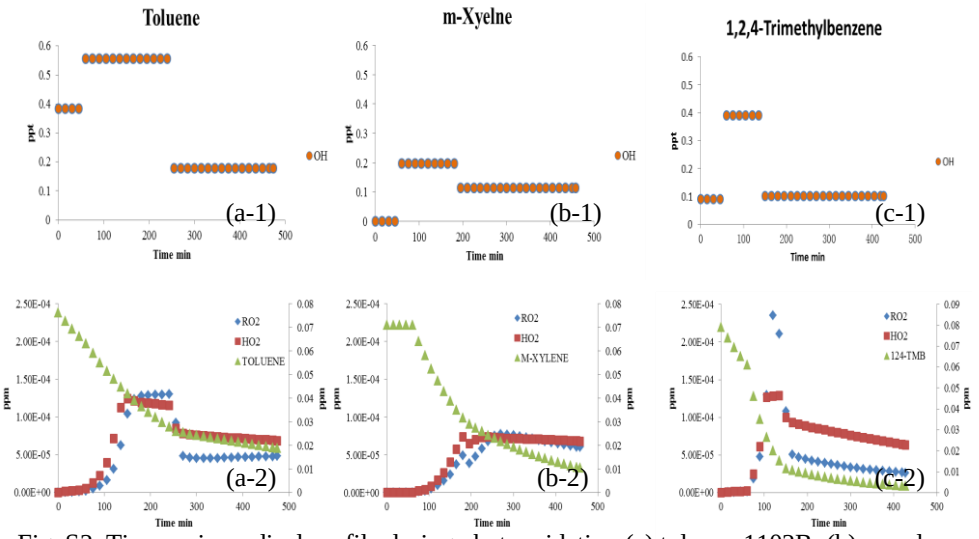


Fig. S2. Time series radical profile during photooxidation (a) toluene 1102B; (b) *m*-xylene 1193A; (c) 1,2,4-trimethylbenzene 1119B)

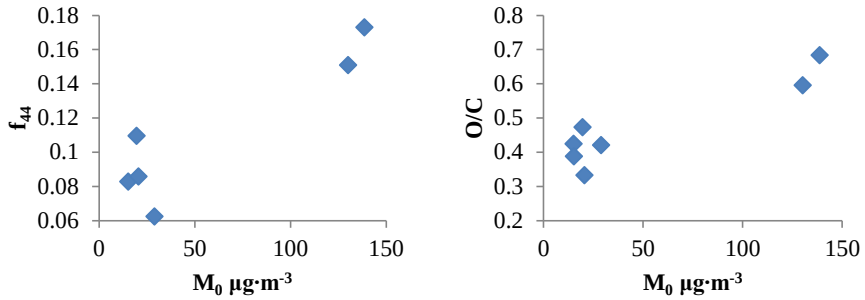
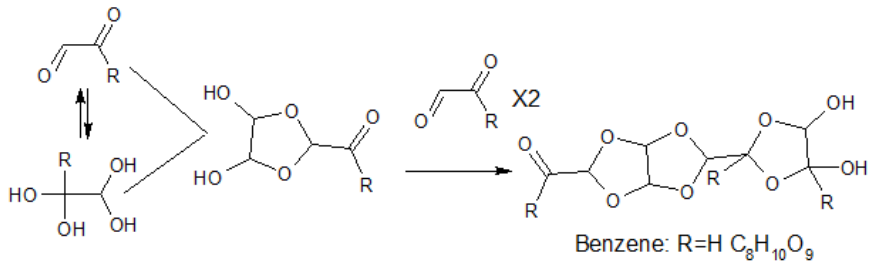


Fig.S3. Relationship between f_{44}, O/C and mass loading

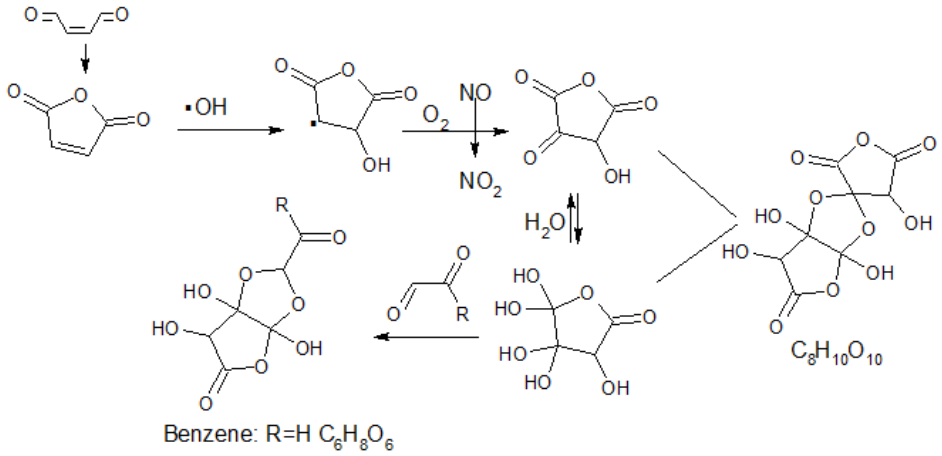
a)

(c-1-1)
or
(c-1-2)



b)

(c-2-1)



(c-2-2)

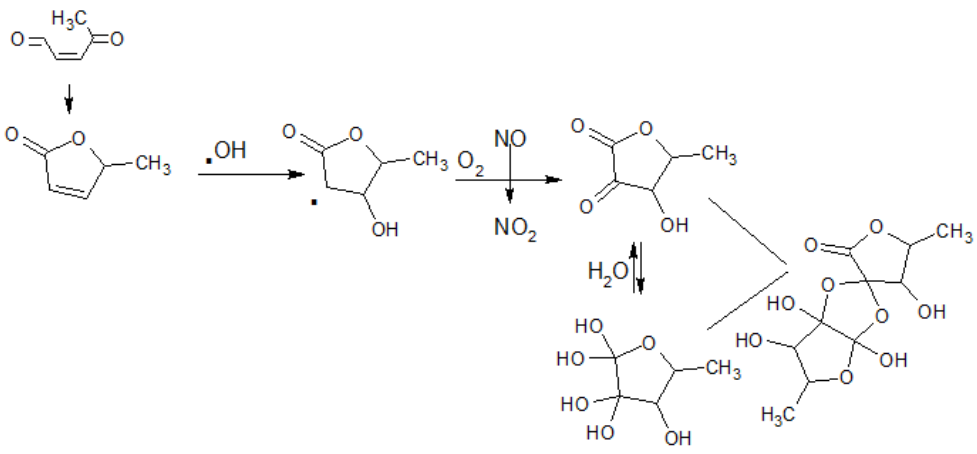


Fig. S4. Potential oligomerization pathways during aromatic hydrocarbon photooxidation a) from saturated 1,2-dicarbonyls to oligomers (adopted from Kalberer, et al, 2004); b) from unsaturated 1,4-dicarbonys to oligomers (c-1-1, c-1-2, c-2-1 and c-2-2 are pathways mentioned in Fig. 7.).

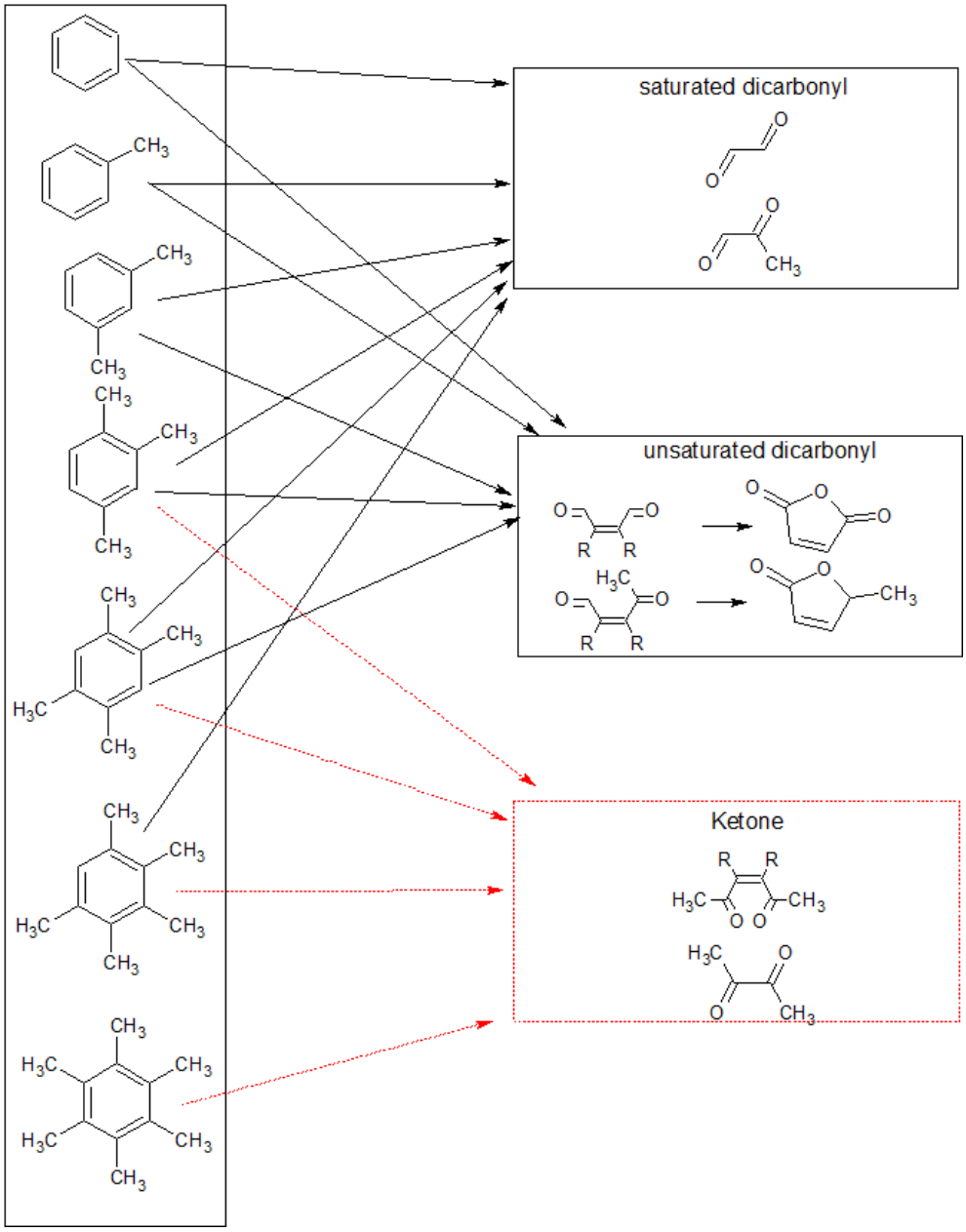


Fig S5. Potential ring opening products of aromatic hydrocarbons during photooxidation (OH attach to ring carbon not occupied by a methyl group is the only pathway considered in pentamethylbenzene photoxidation)